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Thermally Driven Metal Hydride Hydrogen Compressor for Medium-Scale Applications

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Abstract

A promising method of hydrogen compression driven by low-grade heat and not requiring the usage of moving parts, is the application of metal hydrides (MH). However, being upscaled to higher productivities necessary for industrial processes (≥1 m^3 H_2/h STP), the method will inevitably meet a number of problems related to complication of system layout, high costs and significant labour resources for the manufacturing, and low thermal efficiency.
This work presents a development of a prototype MH compressor operating in a temperature range 20 to 150 °C and providing compression of hydrogen from 10 to 200 bar with average productivity up to 1 m^3/h. The compressor realises two stage layout where the first stage uses AB_5- and the second AB_2-type hydride-forming intermetallic alloys. A special engineering solution allows for the usage of quite big MH containers (up to 15 kg of the MH material, or ~2 m^3 STP H_2 capacity), so that the required productivity is provided by just four containers assembled in two compression elements each of which comprises one first- and one second-stage MH containers. The compressor's layout also provides heat regeneration thus reducing the consumption of hot and cold heat transfer fluids and increasing the overall efficiency.

Keywords: Metal hydrides; hydrogen compressor; thermally-driven; two-stage; AB_5; AB_2; development; heat regeneration

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1. Introduction

A promising method of hydrogen compression, which does not require usage of moving parts, is the application of metal hydrides (MH). This method uses thermodynamic features of a reversible heat-driven interaction of a hydride-forming metal, alloy or intermetallic compound with hydrogen gas to form a metal hydride (Fig.1). In so doing, exothermic formation of the metal hydride is accompanied by absorption of low-pressure (P_L) hydrogen in the hydride-forming material, during heat removal therefrom at a lower temperature, T_L. Alternatively, endothermic decomposition of the MH is accompanied by desorption of high-pressure (P_H) hydrogen therefrom, during heat supply to the MH at a higher temperature, T_H. By such a way, periodic cooling / heating of the MH material results in periodic low-pressure hydrogen absorption / high pressure hydrogen desorption, similarly to suction and discharge processes in a mechanical compressor. During the compression cycle (ABCD) carried out in the temperature range T_L to T_H, hydrogen pressure increases from P_L to P_H that, taking into account exponential increase of the hydrogen equilibrium pressure with the temperature (Fig.1(b)), results in the achievement of quite high compression ratio, P_H / P_L ~ 5…10, at (T_H – T_L) ~ 100 K. The cycle productivity of the H_2 compression will be proportional to the reversible hydrogen concentration in the MH (ΔC in Fig. 1(a)) and, as a rule, exceeds 100 L H_2 STP per 1 kg of a hydride-forming alloy.

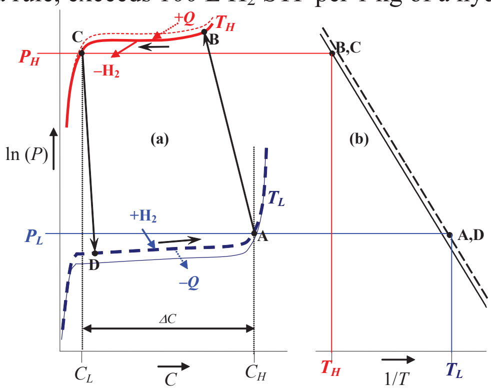

Fig. 1. Schematic representation of thermally driven hydrogen compression using MH: (a) hydrogen absorption (solid) and desorption (dashed) isotherms at lower (T_L) and higher (T_H) process temperatures; (b) temperature dependencies of plateau pressures (Van't Hoff plots) for hydrogen absorption (solid) and desorption (dashed)

When utilising MH, a waste industrial heat having low temperature potential (below 150–200 °C), rather than electric power, can be used for hydrogen compression that increases total efficiency of the industrial process and indirectly contributes to a reduction of greenhouse gases and other harmful emissions to be a by-product of generation electricity at thermal power plants utilising fossil fuels.

The engineering solution realising heat-driven hydrogen compression by the usage of MH was patented in 1970 by Wiswall and Reilly [1] as a method of storing hydrogen where hydrogen gas is absorbed by a titanium-iron alloy at the lower temperature, T_L=10 °C and the lower pressure, P_L~35 bar, and then desorbed at the higher pressure, up to P_H=250 bar, being heated to the higher temperature, up to T_H~200 °C. This solution provided a periodically operated hydrogen compression that restricted its applications in continuous technological processes.

In 1980th the method of heat-driven hydrogen compression using MH was further improved to provide quasi-continuous operation. The corresponding engineering solutions [2] used, as a rule, pairs of identical assemblies of MH containers whose hydrogen inlets / outlets were connected to hydrogen suction and discharge pipelines through one-way (check) valve arrangement, and the periodic heating / cooling of the assemblies was provided in antiphase, so as when one assembly in the pair was heated, another one was cooled and vice versa. Furthermore, application of several assemblies of MH containers filled with hydride-forming materials characterised by different thermal stabilities allowed to realise a multistage layout of the MH compressor and to achieve a high compression ratio in a narrow temperature range. An example of layout of two-stage permanently operated MH compressor utilising more stable, or "high-temperature" (HT), and less stable, or "low-temperature" (LT), MH in the first and second stage, respectively, is shown in Fig. 2. The continuous operation is provided by periodic heating and cooling of two compression elements (CE1, CE2) in the opposite phase. In doing so, low-pressure hydrogen (P_L) is absorbed in the first-stage MH material (HT MH) in the cooled compression element (e.g., CE1). At the same time, heating of the HT MH in the opposite element (CE2) stimulates hydrogen desorption at $P_M > P_L$ followed by its absorption in the LT MH in the second-stage containers of the cooled CE1. Finally, heating of the second-stage container in CE2 causes desorption of high-pressure hydrogen from the LT MH and its output at $P_H > P_M$. Due to rather high pressure differences in gas lines of the compressor, the gas flows are automatically switched by the check valves (shown in Fig. 2 as arrows, filled for the closed valves), and the periodic heating / cooling during pre-set time provides sufficient control of the operation.

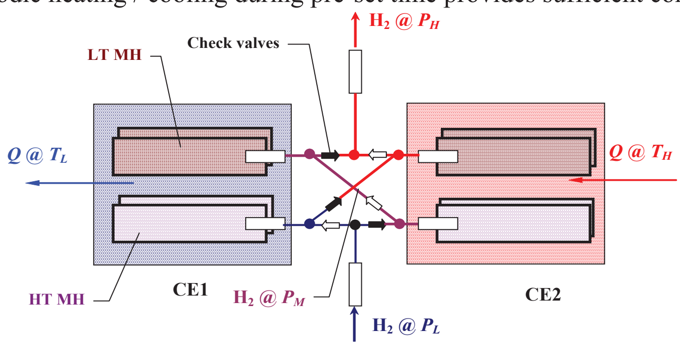

Fig. 2. Layout of two-stage permanently operated MH compressor

At present, thermally-driven compression using MH is a well-approved technology which allows to compress H_2 gas with a productivity up to tens m^3 / h STP [3,4]. The maximum H_2 pressures achievable within this technology are as high as 400…700 bar [5,6] and even 4…5 kbar [7,8].

At the same time, MH compressors, as heat engines, have quite low efficiency [9,10] which, moreover, decreases significantly with an increase of number of stages [11]. Thus the key issue in the development of a MH H_2 compressor for industrial applications is a proper selection of MH materials, to provide specified operation pressures (up to 200 bar that is filling pressure for standard gas cylinders) in temperature range corresponding to an available waste heat source. Operation between ambient temperatures (T_L) and 120…150 ^oC (T_H) is the option available in the industry, including power engineering where spent steam and super-heated water having similar temperatures are available.

Another issue is design of MH containers providing safe, reliable and efficient operation. In addition, the optimisation problems associated with the total compressor's layout and the operational conditions should also be addressed.

The objective of this study is to develop a MH H_2 compressor potentially satisfying the requirements of industrial consumers in terms of:

- Providing necessary H_2 discharge pressure (up to 200 bar) and productivity (x 1 m^3/h);

- Operation using available infrastructure for heating (steam, water; $T_H \leq 150$ °C) and cooling (water; T_L=25…50 °C);
- Competitive cost / performance / service requirements.

Here we present results of the development of a prototype MH compressor operating in a temperature range 20 to 150 °C and providing compression of hydrogen from 10 to 200 bar with average productivity up to 1 m^3/h.

2. Results and Discussion

Earlier [12] we presented a laboratory-scale prototype MH compressor which provided H_2 compression from 7 to 200 bar with a productivity about 60 L/h STP. The required hydrogen compression was achieved in the temperature range from 15…25 to 110…130 °C, by the application of two-stage layout using AB_5-type intermetallic alloy (160 g) for the first and AB_2-type one (120 g) for the second stage. These results became a basis for the present development described below.

2.1. MH materials

Analysis of hydrogen absorption / desorption properties of MH materials potentially satisfying to the application requirements showed that the AB_5 alloy, where A=Ce (15 at.%) + La (balance), B=Ni; exhibits satisfactory performances for the operation at the first stage of the compressor. The selected composition of AB_2-type material for the second stage was quite close to the one used in the previous study [12] and corresponded to hypo-stoichiometric formula AB_{2-x}, where A=(Ti+Zr), B=(Mn+Fe+Cr+Ni), x~0.1; the alloy exhibited C14 ($MgZn_2$-type) intermetallic structure with lattice periods *a*=4.898 Å, *c*=8.019 Å. The batches of 100 kg of both AB_5- and AB_2-type alloys specified for the project were manufactured by a Chinese industrial company and supplied in a powdered form.

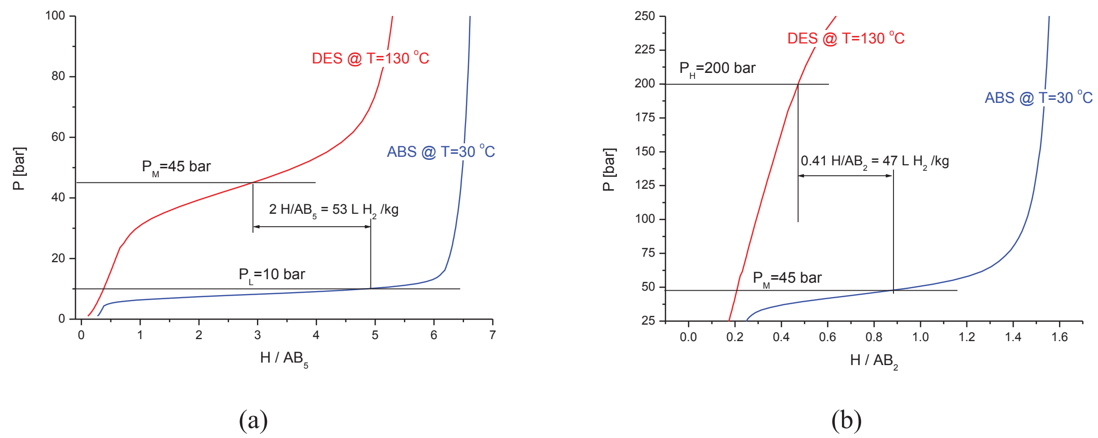

Fig. 3. PCT characteristics of the AB_5- (a) and AB_2-type (b) materials used for the first and second stages of H_2 compressor

Fig. 2 presents isotherms for hydrogen absorption at T_L=30 °C and hydrogen desorption at T_H=130 °C for AB_5- (a) and AB_2-type (b) MH materials used in the compressor. The experimental PCT data were collected in the range *P*=1–180 bar and *T*=0–150 °C using PCTPro–2000 automated gas sorption analyser (Hy-Energy Scientific Instruments) and further processed using a model of phase equilibria in metal – hydrogen systems by Lototsky et. al. [13]. As it can be seen from Fig.3, the operation in the specified pressure – temperature ranges allows to achieve an average cycle productivity corresponding to about 50 L H_2 STP per 1 kg of the MH material; in doing so the intermediate pressure in between the first and second stages is about P_M=45 bar.

The safe load of the materials into MH containers which was shown to be below 60% of real density of the material in the hydrogenated state [14] was determined from XRD data for the alloys hydrogenated at P_{H2}=80 bar and room temperature and further stabilised by 5 minutes-long exposure to air at 77 K. The densities were calculated as 6.7 and 5.5 g/cm^3; so that the filling densities were set to be 3.5 and 2.9 g/cm^3 for AB_5 and AB_2, respectively, or about 52% of the real density of the hydrogenated alloy.

2.2. Layout of the compressor and MH containers

The MH compressor realises two stage layout, where the first stage uses AB_5- and the second – AB_2-type hydride-forming materials described above. A special engineering solution ([15]; Fig 3) allows for the usage of quite big MH containers (~2 m^3 STP in H_2 capacity), so that the required productivity is provided by four containers assembled in two compression elements each of which comprises one first- and one second-stage MH containers. The compressor's layout also provides heat regeneration thus reducing the consumption of hot and cold heat transfer fluids and increasing the overall efficiency.

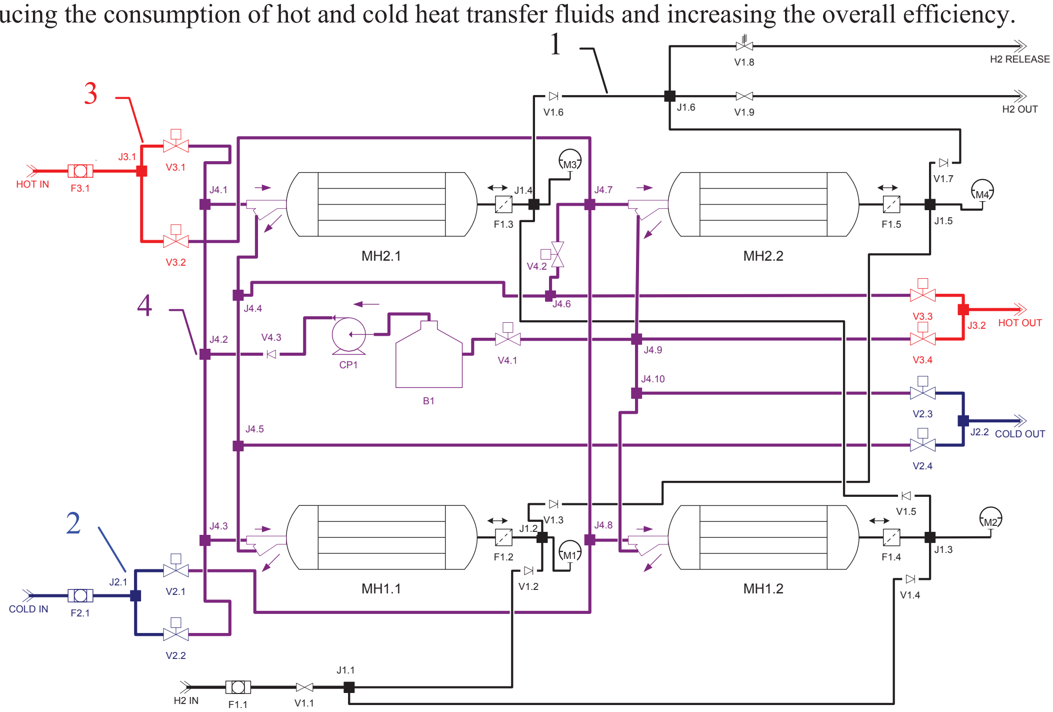

Fig. 4. Layout of the MH compressor: MH1.1, MH1.2 – MH containers of the first stage, compression elements 1 and 2, respectively; MH2.1, MH2.2 – MH containers of the second stage, compression elements 1 and 2, respectively; 1 – gas pipelines, valves and fittings; 2 – cold fluid system; 3 – hot fluid system; 4 – heating / cooling and heat regeneration loop.

Main parts of the compressor include two first stage (MH1.1, MH1.2) and two second-stage (MH2.1, MH2.2) MH containers equipped with in-line gas filters (F1.2–F1.5); the gas manifolds of the compression elements are connected to manometers (M1–M4) for separate measuring the corresponding hydrogen pressures and, via the system of check valves (V1.2–V1.7), to the low pressure suction line and high pressure discharge line equipped with shut-off valves (V1.1, V1.9). The high-pressure line additionally comprises safety relief valve (V1.8) for the release of hydrogen in the case of overpressure. The compressor also has the systems for supply, distribution and removal of cold (2) and hot (3) heat transfer fluids, as well as internal heating / cooling circulation loop (4); managing the flows of the heat transfer fluids is provided by solenoid valves (V2.1–V2.4, V3.1–V3.4, V4.1–V4.2), check valve (V4.3), circulation pump (CP1), buffer tank (B1) and other fittings. The compressor can use various combinations of cooling / heating fluids (water / steam, water / superheated water, oil); to provide cooling, T_L~15 °C, and heating, T_H~130 °C, temperatures.

The operation of the compressor is provided using a PLC-based control block, by periodic alternative heating / cooling of two compression modules first of which is formed by MH1.1 and MH2.1, and the second by MH1.2 and MH2.2. The heating and cooling is provided by opening / closing the solenoid valves during the pre-set period of time (20…45 minutes). In addition, before switching between heating and cooling, a 1…5 minutes long circulation of the heat transfer fluid through the circulation loop is carried out, to provide temperature equilibration between hot and cold MH containers. The circulation is provided by switching on circulation pump (CP1), and opening solenoid valves (V4.1, V4.2).

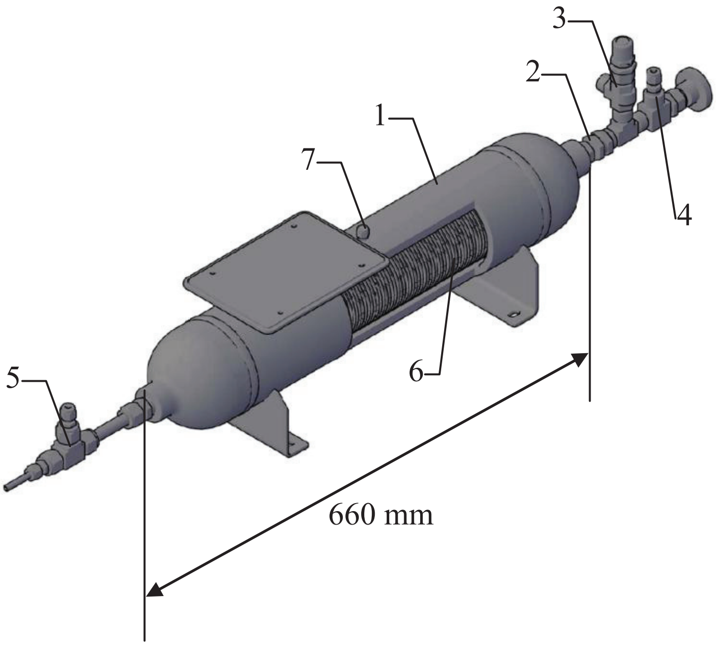

Fig. 5. Metal hydride container.

Fig 5 shows the assembly drawing of the MH container for the compressor [15]. The containers were built by Unique Hydra (PTY) LTD according to ASME VIII DIV 1 2007 (A09) and certified according to South African safety regulations (RSA/CIF 81-07-A09; 200 bar at 200 °C). Both stage 1 and stage 2 containers have similar layouts comprising cylindrical external shell (1; SS316 seamless tube, Ø114.3x8.56 mm) equipped with two hemispherical end caps. One of the end caps carries gas supply and removal fittings, including in-line gas filter (2), a gas manifold with a safety relief valve (3) and shut-off valve (4) with hydrogen input / output connecting pipe. The opposite end cap is fitted with a “tube in tube” internal heat exchanger comprising an external / core tube (SS316 seamless, Ø12.7x2.15 mm), an internal tube (SS316 seamless, Ø6.35x0.89 mm), a manifold (5) for input and output of a heating /

cooling fluid (5), and lamellar copper fins (6) distributed inside the container with a step about 10 mm. The weight of the empty container is about 19 kg, and the load of the MH material – about 15 and 12 kg for AB_5 and AB_2, respectively.

One of four MH containers (two for the first and two for the second stages), namely MH1.2 (Fig.4) was equipped with three fittings (7 in Fig 5) carrying thermocouples TC1, TC2 and TC3, for measuring temperatures in the MH bed in the middle of the container at the distance from the outside of the core tube of the internal heat exchanger of 6, 22 and 35 mm, respectively.

2.3. Testing facilities and procedure

A specially designed testrig (Fig.6) allowed us to test both separate MH containers (in H_2 absorption and desorption modes switched by valves V2 and V3) and MH compressor, in the pressure range 1 to 200 bar, at H_2 flow rates up to 6 m^3/h. The tested units were connected to gas-distributing system comprising evacuation and external H_2 supply lines, connecting pipelines, buffer cylinder, pressure-reducing regulators, back-pressure regulator, motorised 3-way valves, pressure and flow sensors.

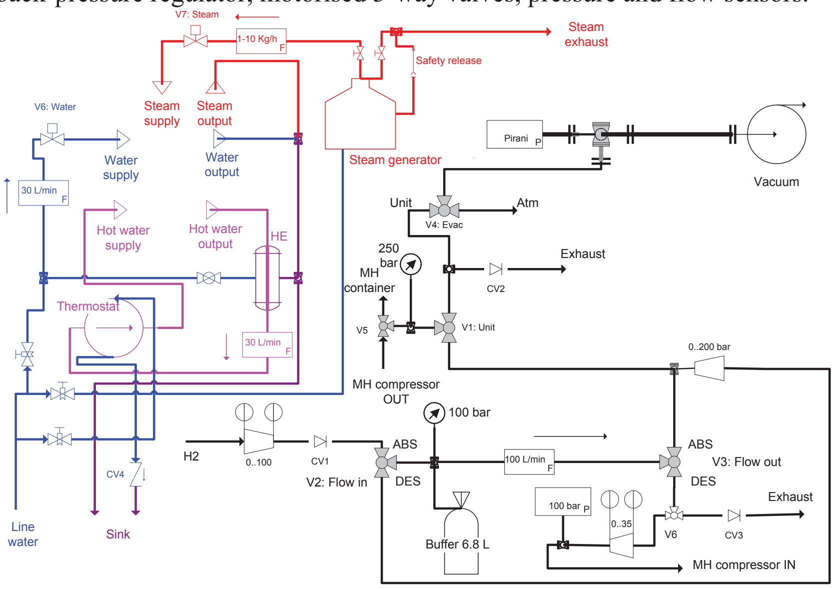

Fig. 6. Piping diagram of the testrig.

During testing of MH containers in H_2 absorption mode, hydrogen was supplied from external line at the pressure of up to 100 bar set by the reducer; the pressure of hydrogen desorption (10 to 200 bar) was set by the back-pressure regulator, the excess H_2 was released into exhaust line. Tests of the MH compressor were carried out in a stationary circulation mode (valves V2 and V3 switched to DES position), with suction pressure, *P*(in), varied within 10…35 bar (using additional reducer) and discharge pressure, *P*(out), – within 100…200 bar (using the same back-pressure regulator). Cooling of the MH container / compressor was provided by a tap water (temperature 15…25 ^oC; controlled flow rate up to 20 L/min). The heating system included supply of a wet steam (temperature up to 140 ^oC; flow rate up to 10 kg/h), or circulation of superheated water (temperature up to 180 ^oC; flow rate up to 20 L/min). In addition, a flow meter was installed in the gas system of the compressor measuring flow rate of H_2 from first to second stages (from MH1.2 to MH2.1; Fig.4).

All the process parameters (temperatures, flow rates of heating / cooling fluid and hydrogen, hydrogen pressures) were collected by a data acquisition system with LabView interface.

2.4. Test results

Table 1 summarises results of testing the MH containers (steam heating 120 ^{o}C / 9 kg/h; water cooling 15 ^{o}C / 5 L/min).

Table 1. Summary of test results of MH containers

Stage	Process / pressure [bar]	Charge / discharge productivity [m^3/h] (t=90 min)	
		Peak	Average
1	Absorption / 10 bar	3.26	1.31
	Desorption / 60 bar	1.56	1.03
2	Absorption / 60 bar	0.96	0.71
	Desorption / 200 bar	>3.3	0.70

According to the test results, the total productivity of H_2 compression will be mainly limited by the charge of 2nd stage MH.

The compressor under testing is shown in Fig 7. Fig 8 presents typical test results taken in the course of 29 minutes-long steam heating (8.5 kg/h) / water cooling (5.3 L/min) followed by 1 minute-long circulation stage. Replacement of steam with superheated water somewhat increases the compressor's productivity, but this effect is not very significant, since the total productivity of the compressor, first of all, is limited by slow suction processes at the first (FR(in)) and, especially between first and second (FR(mid)) stages. Acceleration of these processes could be achieved by the intensification of cooling the MH containers down.

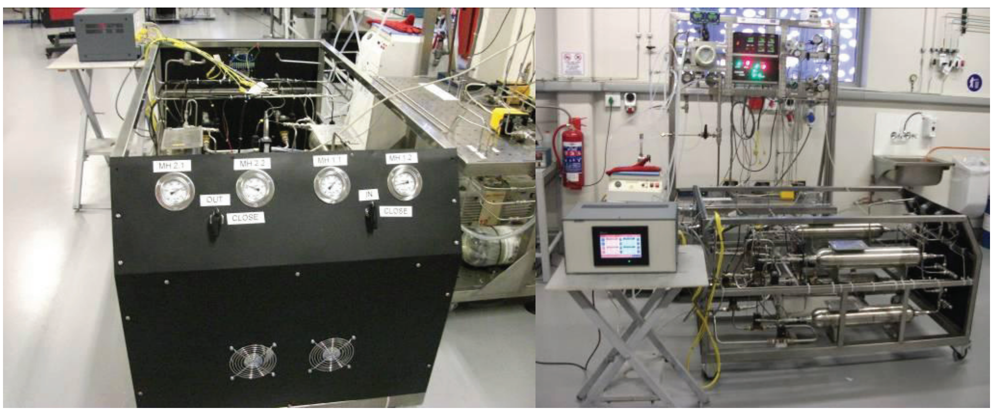

Fig. 7. Testing of the MH compressor.

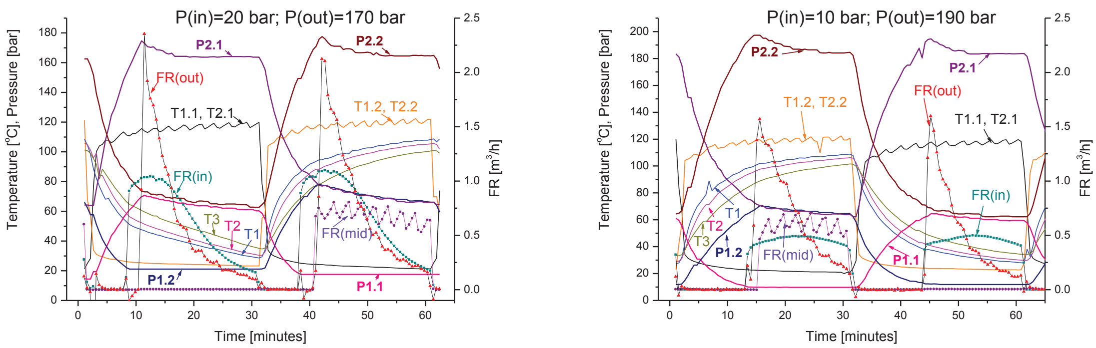

Fig. 8. Testing results:

- P1.1, T1.1 … P.2.2, T2.2 — Pressures and heating / cooling temperatures for the corresponding MH containers (Fig.4);
- T1, T2, T3 — Temperatures within MH bed of the container MH1.2 (TC1, TC2, TC3, respectively);
- FR(in) — Hydrogen input flow rate;
- FR(out) — Hydrogen output flow rate;
- FR(mid) — Hydrogen flow rate between stages 1 and 2.

Depending of the operating conditions (first of all, H_2 input pressure and cycle time), the productivity of the compressor varies within 400…800 L/h STP and approaches to 1 m^3/h at $P_L \geq 20$ bar.

3. Conclusions and Future Plans

- Thermally-driven metal hydride hydrogen compressor providing H_2 compression from 10…20 to 200 bar with the average productivity up to 1 m^3/h was developed and tested.
- The compressor realises two stage layout where the first stage uses AB_5- and the second AB_2-type hydride-forming intermetallic alloys.
- The compressor requires cooling by water at T=15…25 ^oC and heating by low-grade steam or superheated water at T=120…140 ^oC.
- The productivity of the compressor, first of all, is limited by H_2 suction processes at the first and, especially, between the first and the second stages.
- The productivity drops when decreasing H_2 input pressure and, in a lesser extent, when the H_2 output (discharge) pressure increases.
- Improvement of heat exchange between MH bed and heating / cooling fluid (especially, in the course of cooling) may result in the increase of the productivity.
- The developed engineering solutions will be further optimised followed by upscale to 5-10 m^3/h.

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